# Stability of crystal surfaces: faceting

In this chapter we want to examine the stability of surfaces with respect to small deviations of their orientation. If a crystal surface is prepared initially with an orientation that is between two more stable orientations according to the Wulff diagram, will the surface decompose into facets of these more stable orientations ?

If this happens the new surface will have the appearance of a hill and valley structure with the same average orientation:
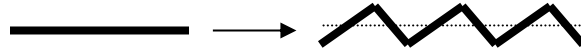

The sides of the hills should be orientations of higher stability.

The following treatment, due to Prof. N. Cabrera (Symposium on Properties of Surfaces, Special Technical publication No. 340. American Society for Testing and Materials, 1962), treats this problem as one similar to the equilibrium between bulk phases, the phases here being the new facets.

The change in the thermodynamic free energy potential (here we use the Ω potential), for a volume-conserving transformation where the surface A into A' is:

$$\Delta\Omega = \int_{A'} \gamma(\vec{n}')dA' - \gamma(\vec{n}).A$$
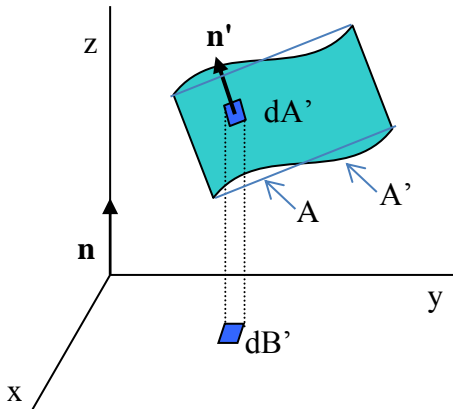
Let the new surface A' be described by the function z = z(x,y).

The vector gradient: $(-\dfrac{\partial z}{\partial x}, -\dfrac{\partial z}{\partial y}, 1) = (p, q, 1)$ is perpendicular to it, with p and q being the tangents of the orientation angles, which we chose as the parameters of the surface tension function γ, instead of the angles because, as we will see, it simplifies the math. We define a vector **p** in the xy plane with components (p,q,0). We have therefore,

$$\vec{n}'\sqrt{1+p^2+q^2} = \vec{n} + \vec{p}$$

Where **n'** and **n** are the unit vectors perpendicular to A' and A respectively. The projected area dB' is:

$$dB' = dA'.\cos\theta = \frac{dA'}{\sqrt{1+p^2+q^2}}$$

We will work with projected areas and define the surface tension *per unit projected area* $\beta(p,q)$. We use the notation (p,q) or **p** or p with an arrow indistinctly. The relation between γ and β is simply:

$$\beta(\vec{p}) = \gamma(\vec{p}).\sqrt{1+p^2+q^2}$$

So can we write:

$$\Delta\Omega = \int_{A'}\beta(\vec{p}')dB' - \beta(\vec{p}).B \qquad (1)$$

As we discussed before the function $\beta(p,q)$ has a cusp singularity at the orientation of low Miller index surfaces, which include the (111) and (100) planes of fcc materials, the (110) of bcc and the basal, or (0001) planes of hcp. The function $\beta(p,q)$ looks something like the graph in the figure,
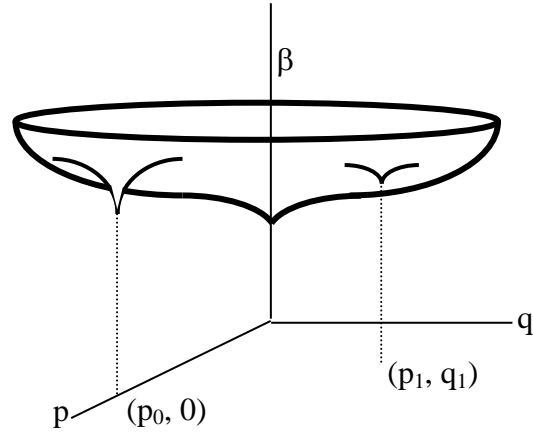
with three cusps drawn for three hypothetical singular surfaces. Outside the singularity, $\beta(p,q)$ can be expanded:

$$\beta(\vec{p}') = \beta(\vec{p}) + \frac{\partial\beta}{\partial\vec{p}}\cdot\delta\vec{p} + \frac{1}{2}\delta\vec{p}\left[\frac{\partial^2\beta}{\partial\vec{p}^2}\right]\delta\vec{p} + ... \qquad (2)$$

The third term in (3) is a quadratic form of second order. It can be diagonalized by a transformation of the axis along its eigenvectors:

$$\begin{pmatrix} \dfrac{\partial^2\beta}{\partial p^2} & \dfrac{\partial^2\beta}{\partial p\partial q} \\ \dfrac{\partial^2\beta}{\partial p\partial q} & \dfrac{\partial^2\beta}{\partial q^2} \end{pmatrix} \rightarrow \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

The eigenvectors point in the direction of the principal axis (principal curvatures) and the eigenvalues are the local curvatures λ_1 and λ_2. With this transformation of coordinates, (2) becomes:

$$\beta(\vec{p}') = \beta(\vec{p}) + \frac{\partial \beta}{\partial \vec{p}} \cdot \delta\vec{p} + \frac{1}{2}\left[\lambda_1(\delta p_1)^2 + \lambda_2(\delta p_2)^2\right] + \dots \quad (3)$$

Upon substitution into (1) the first term in (3) cancels and the integration of the second term is zero because of conservation of the average orientation:
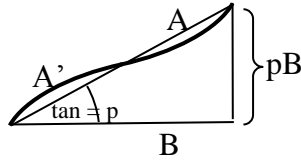
$$\int_B dB' = B \qquad \text{and} \qquad \int_B \delta\beta \cdot dB' = pB$$

Finally we obtain:
$$\Delta\Omega = \frac{1}{2}\left[\lambda_1 \int_B (\delta p_1)^2 dB + \lambda_2 \int_B (\delta p_2)^2 dB\right]$$

This tells us that if the curvatures are positive ($\lambda_1 > 0$, $\lambda_2 > 0$) the surface is stable, since any change leads to an increase in Ω. If either λ_1 or λ_2 is negative, the new orientation is unstable, and such a surface will decompose into two or more stable surfaces. This situation is similar to that of an unstable volume phase that will break up into two or three phases.

Stable unstable
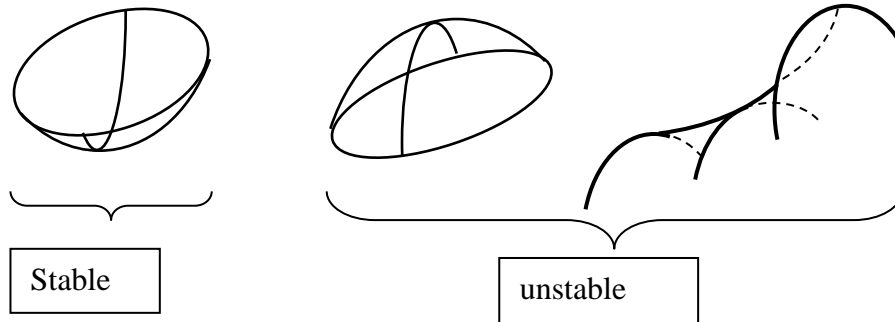
The following graphical construction helps visualize the orientation of the stable surface orientations into which the original surface decomposes. The $\beta(p,q)$ function is shown in two dimension by the red curves. To determine the two stable orientations we draw a plane inside the Wulff surface tension curve and bring it up (along the β axis) until it touches tangentially $\beta(p,q)$, which will happen in three points (two only can be

shown in the 2D plot of the figure below). These points, p_o, p_1 near the cusp (left), and p_1, p_2, away from the cusp (right) are the orientations of the stable surface forming the hill and valley structure of the reconstructed surface.
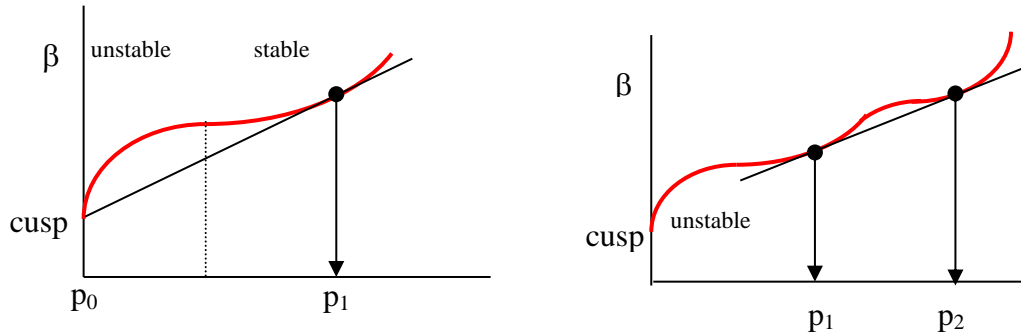
Adsorption of gases can change the shape of $\gamma(\theta)$, because it changes the surface tension, particularly it changes the energy of the step atoms, which can change their interaction from repulsive to attractive, to giving rise to restructuring of the surfaces.

The stereographic diagrams below (Somorjai) shows how the stability of Pt(111) stepped surfaces changes with adsorption of O and C.
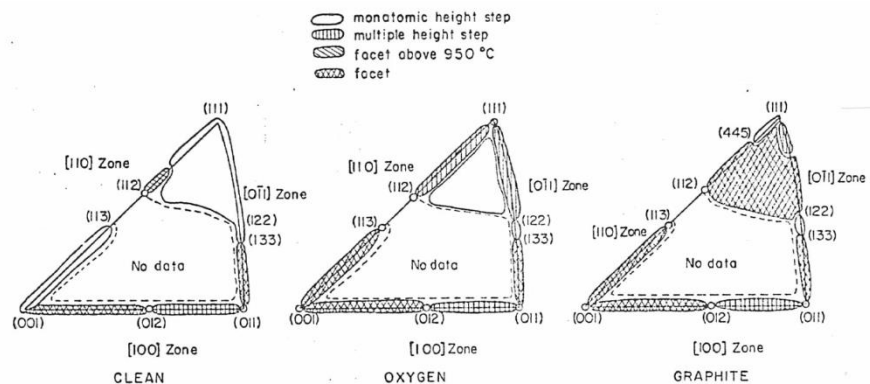
The following STM images show how the surface structure of Pt(110) changes with different chemisorbed gases (from B.J. McIntyre, M. Salmeron and G.A. Somorjai. J. Vac. Sci. Technol. A. 11 (4), 1964 (1993)):

The structure of Pt(110) in equilibrium with various gases

1.6 atm of H_2:
Missing row
reconstructions

1 atm of O_2:
Faceting into (111) vicinal
planes

1 atm of CO: Step bunching